

X-691-74-151

PREPRINT

NASA TM X- 70662

LASER MEASUREMENTS OF THE RADIATIVE LIFETIME OF THE B STATE OF CN

(NASA-TM-X-70662) LASER MEASUREMENTS OF
THE RADIATIVE LIFETIME OF THE B STATE OF
CN (NASA) 25 p HC \$4.25 CSCL 20E

N74-25992

G3/16

Unclas
40321

W. M. JACKSON

MAY 1974

GSFC

GODDARD SPACE FLIGHT CENTER

GREENBELT, MARYLAND

**For information concerning availability
of this document contact:**

**Technical Information Division, Code 250
Goddard Space Flight Center
Greenbelt, Maryland 20771**

(Telephone 301-982-4488)

LASER MEASUREMENTS OF THE RADIATIVE
LIFETIME OF THE $B^2\Sigma^+$ STATE OF CN

W. M. Jackson
Astrochemistry Branch
Laboratory for Extraterrestrial Physics
NASA/Goddard Space Flight Center
Greenbelt, Maryland

ABSTRACT

A tunable dye laser has been used to measure the radiative lifetime of the individual rotational levels of the $B^2\Sigma^+$ state of CN. The radiative lifetime of the unperturbed rotational levels is 65.6 ± 1.0 nsec in agreement with previous workers. A longer radiative lifetime of 72 ± 1 nsec is observed for the $K' = 4$ level of the B state. The measured values of the perturbed and unperturbed levels support the longer lifetimes for the $A^2\Pi$ state of CN. The quenching cross section of the $B^2\Sigma$ state of CN is $41 \pm 20 \text{ \AA}^2$ and is independent of the rotational energy of the B state.

LASER MEASUREMENTS OF THE RADIATIVE
LIFETIME OF THE $B^2\Sigma^+$ STATE OF CN

W. M. Jackson
Astrochemistry Branch
Laboratory for Extraterrestrial Physics
NASA/Goddard Space Flight Center
Greenbelt, Maryland

INTRODUCTION

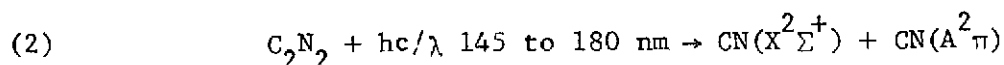
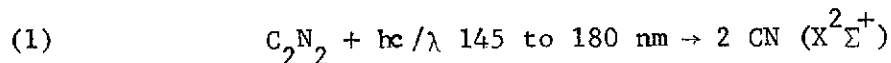
The CN radical is an important constituent in many systems such as comets, the interstellar medium, flames and stellar atmospheres. In all of these systems the $B^2\Sigma^+ \leftrightarrow X^2\Sigma^+$ transition is observed in absorption or emission and the strength of the transition is used to determine the concentration of the radicals in the system. The accuracy of these concentration measurements depend upon our knowledge of the transition probability of the band which in turn is determined by the radiative lifetimes of the system. Measured radiative lifetimes of the $B^2\Sigma^+$ state differ by as much as a factor of 2, although the more recent measurements of Liszt and Hesser¹ and Luk and Bersohn² are in agreement with one another. All of the measurements except those of Cook and Levy³ depend upon the formation of the $B^2\Sigma^+$ state via dissociative excitation of stable molecules using photon or electron impact techniques. Neither technique produces the radicals with a known rotational distribution so that if the lifetime varies among the rotational levels the measurements can be biased. Herzberg⁴ has shown that several rotational levels of the B state are perturbed by the $A^2\Pi$ state and should have a radiative lifetime longer than the unperturbed levels. The observed lifetimes can be biased if the

the dissociation process preferentially produces the B state in the perturbed rotational levels. In fact the only measured $B^2\Sigma^+$ state lifetime which does not depend on a dissociative excitation method is 39 nsec which is considerably shorter than the other lifetime measurements. It is therefore of interest to determine the radiative lifetime of the $B^2\Sigma^+$ state of CN in a way that will not be influenced by the effects of these perturbed rotational levels.

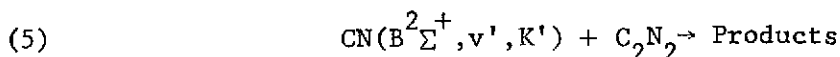
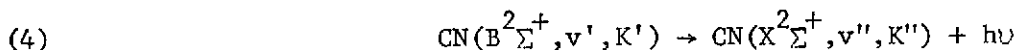
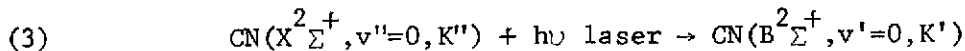
The direct excitation of each rotational level with a suitable pulsed light source is an independent method for determining the radiative lifetime. Because of their high reactivity it is difficult to obtain high concentrations of CN radicals so that this method requires a high intensity, narrow bandwidth, tunable light source in the near ultraviolet region in order to achieve suitable signal to noise ratios. A nitrogen laser pumped tunable dye laser is such a light source and has been used in the present work along with a low intensity vacuum ultraviolet flash lamp to measure the radiative lifetime of individual rotational levels of the B state of the CN radical.

THEORY

The CN radicals are produced in the $X^2\Sigma^+$ or $A^2\Pi$ by the flash photolysis of C_2N_2 in its first strong absorption band between 150 nm and 180 nm. This is represented by the following possible photochemical reactions,



Any radicals that are produced in the $A^2\pi$ state will have had ample time to radiatively decay or be quenched to the X state during the 100 μ sec delay that occurs between the laser and the flash lamp pulses. When the laser is pulsed the X state radicals are excited to the B state which can then either radiate or be quenched by collisions with C_2N_2 . This sequence of events is represented by reactions (3) through (5).



The time dependence of the fluorescent light intensity, I_f , from reaction (4) is given by equation (1). The slope of a semilogarithmic

$$(1) \quad I_f = I_f^0 e^{-t/\tau}$$

plot of I_f versus time yields τ . The functional relationship between this measured lifetime and the true radiative lifetime $\tau_{K'}^0$ is given by

$$(2) \quad \frac{1}{\tau} = \frac{1}{\tau_{K'}^0} + k_{qK'} P_{C_2N_2}$$

where $k_{qK'}$ is the quenching rate constant at the given pressure ($P_{C_2N_2}$) of C_2N_2 . Measuring τ as a function of $P_{C_2N_2}$ and plotting the results in accordance with equation (2) will yield a straight line whose intercept is the desired radiative lifetime of the K' level.

EXPERIMENTAL

A schematic diagram of the apparatus is given in Figure 1. The dye laser was constructed using the basic design of Hansch.⁵ A saturated

solution of BBD (Bi-biphenyloxadazole) in toluene yielded a laser output of 10^{12} to 10^{13} photons per pulse with a bandwidth of 0.012 nm, measured with a Fabry-Perot etalon. The laser beam was first expanded with a X3 beam expander, passed through a polarizer and a half-wave Frensel rhomb and then focused into the reaction cell with a long focal length lens. The fluorescent intensity did not depend on the direction of polarization, so that the direction of polarization was chosen to minimize the reflected light from the Brewster windows on the fluorescence cell.

The fluorescence cell was a 5- cm cube with two 50 cm arms on opposite faces of the cube through which the laser light entered and left the cell. These arms contain fifty baffles placed one centimeter apart which are effective in reducing both scattered laser and room light. One face of the cube serves as a pumping port while the other face serves as an entrance port for the cyanogen used in this study. The face of the cube opposite the pumping port had a sapphire window for the entering vacuum ultraviolet light. This light had been collimated by a piece of black delerin with coarse screw threads. The final face of the cube had a pyrex window which allowed some of the fluorescent light from the cell to pass through two interference filters centered at $4216\overset{\circ}{\text{\AA}}$. This light strikes the photocathode of an RCA 8850 photomultiplier tube operated at 1800 volts which converts the photon signal to a charge pulse for the photon counting system.

The charge pulse that is generated by the photon is transmitted by a 50 ohm cable to the input of a amplifier driving the input of a fast discriminator. These components were chosen for both their speed and fast recovery from any overloads. After passing through the discriminator the pulse was further amplified by another amplifier before going to the input of a Davidson time of flight unit. This unit was triggered by a delayed trigger pulse generated by an E.G&G lite mike which picks up the light from the ultraviolet flash lamp. The time of flight unit has four output buffer memories which allow up to 4 photons to be counted after each laser pulse. The counts are transferred to a multichannel analyzer operating in the pulse height analysis mode and accumulated until a good signal to noise ratio is obtained. This system gives a time resolution of 10 nsec per channel. The data from the multichannel analyzer is read out on a teletype and then punched on cards for further analysis.

The vacuum ultraviolet flash lamp used in these studies was similar to the design of Braun et al.⁶ It consisted of a teflon body with stainless steel tip electrodes placed about a millimeter apart. A Xenon Corp. power supply which had a built in oscillator and could supply up to 5 joules per flash at 100 flashes per second was used to power the lamp. For all of the experiments reported in this paper the lamp was operated at 50 cps with a flash energy of 0.8 joules per pulse. Under these conditions the FWHM of the UV flash was two microseconds, and the scattered light from the lamp was only 6×10^{-2} counts per flash at the 100 μ sec delay times used in these studies.

Tank cyanogen supplied by Matheson was purified by passing through P_2O_5 and then pumping on it at both liquid N_2 and solid acetone temperatures. Before each lifetime run the C_2N_2 was frozen in liquid N_2 and pumped on for a few minutes. Cyanogen was then introduced into the fluorescence cell and the pressure measured with a MKS Baratron capacitance manometer. The pressure was kept constant to better than 10% during a run by a Granville-Phillips pressure controller. This in turn kept the fluorescent light intensity constant to within 10% during each run.

The position of a given rotational line was identified by first taking a fluorescent excitation spectra similar to the one shown in Figure 2. The channel number corresponding to the peak of a particular line was identified and the laser tuned to this particular channel. A decay curve was then measured for a particular C_2N_2 pressure. After obtaining this decay curve the pressure of C_2N_2 in the fluorescence cell was changed and the decay curve remeasured. This procedure was repeated for each of the sixteen rotational lines reported in the present work.

RESULTS AND DISCUSSIONS

A. Radiative Lifetime

The curves in Figure 3 are typical examples of the type of data that is obtained in the present experiments. The points in these curves have been corrected for noise counts due to scattered light and dark counts. The first few points corresponding to the initial laser rise time have been discarded and the y axis has been shifted so that zero time corresponds to the peak of the corrected fluorescent curve. The lines through the points are computed from a least squares fitting procedure. This least squares fitting procedure yields a slope

from which the τ in equation (1) can be extracted. When the reciprocal of τ is plotted against the cyanogen pressures, curves of the type reported in Figure 4 are obtained. The intercepts of these curves give the radiative lifetime of each individual rotational level.

Table 1 summarizes the radiative lifetimes for the individual rotational levels of the B state of CN. The errors quoted in this table are for a 2σ deviation calculated by using the statistical errors in the observed number of counts in the least squares fitting program. The bandwidth of the laser is 0.01 nm so that as K' increases overlapping occurs between individual rotational lines in the P branch. Similar overlapping occurs between the rotational levels of the R branch in the 0-0 band and the P branch of the 1-1 band. Because of this blending only one of the perturbed rotational lines ($K' = 4$) is sufficiently resolved to see the effect of perturbations on the radiative lifetime.

The average radiative lifetime of the unperturbed rotational levels is reported in Table 2 along with the radiative lifetimes reported by previous workers. The present results agree reasonably well with the latest measurements of Liszt and Hesser¹ and Luk and Bersohn² although both results appear to yield lifetimes somewhat shorter than the present work. The earlier work of Bennett and Dalby⁷ and Moore and Robinson⁸ both appear longer than the latest direct measurements. One possible explanation is that in this earlier work the perturbed rotational levels were somehow preferentially populated giving longer observed radiative lifetimes. The lifetime reported by Cook and Levy³ is substantially shorter than the other lifetimes and could reflect systematic errors in their measurements.

The radiative lifetime can be used to calculate a f value of the 0-0 transition of the B state. The results of these calculations are compared in Table 3 with the f values calculated from the measurements of other workers. Again the latest values are in substantial agreement with each other and with the absorption measurements in shock tubes of Arnold and Nicholls.⁹

Each of the rotational lines shown in Figure 2 is in reality a doublet (p doublet) both of which have the same parity (i) but a different total angular momentum (J). In the absence of electric and magnetic fields, perturbations can only occur between π and Σ states with the same parity and angular momentum. For the $K' = 4$ level of the B state only one of the P doublets will be perturbed by a λ doublet of the $A^2\Pi_{3/2}$ state. The perturbation theory of Radford and Broida¹⁰ can be used to calculate the lifetime of the perturbed doublet $\tau_{\sigma p}$ from the lifetime of the pure sigma state τ_{σ} , the pure pi state τ_{π} , and the perturbation parameter p^2 using the following expression,

$$\frac{1}{\tau_{\sigma p}} = \text{perturbed sigma lifetime} = \frac{(1-p^2)}{\tau_{\sigma}} + \frac{p^2}{\tau_{\pi}}.$$

The theory also predicts that the initial number density of the perturbed state will only be $(1-p^2)$ of the density of the unperturbed state. With these considerations in mind an expression for the relative intensity of the $K' = 4$ line of the B state may be written as,

$$\frac{I}{I_0} = (1-p^2) \exp(-t/\tau_{\sigma p}) + \exp(-t/\tau_{\sigma})$$

Artificial data points for the various values of τ_{π} in Table 4 can be calculated from this expression by using a value of p^2 of 0.14 and the τ_{σ} determined in this work. These data points were then used with the least squares program to compute lifetimes of the $K' = 4$ level which should be comparable to the lifetimes measured for the $K' = 4$ level.

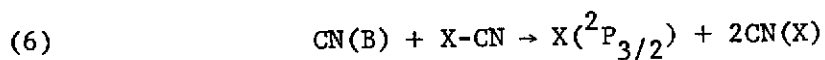
The results of these calculations are reported in Table 4 along with the observed value of the lifetime. The observed lifetime is calculated by averaging the P and R branch lifetimes in Table 1 and the errors were calculated from the deviation from this average. The calculation was made for two initial distributions of the perturbed and unperturbed components of the $K' = 4$ line. The first corresponds to the case in which no collisions have occurred to equilibrate the perturbed and unperturbed levels of the $K' = 4$ state. The observed results are in reasonable agreement with computed lifetimes based upon equilibration among the $K' = 4$ levels and the larger values of the π state lifetime. The larger values of the π state lifetime agree with the lifetime measurements obtained from the solar observations of the CN radiation.¹¹

B. Quenching Cross Section

The slope of the curve in Figure 4 gives the rate constant for quenching via reaction (5). These rate constants are summarized in Table 5 for the various rotational levels of the B state. No systematic trend in the quenching rate constant is observed. The error quoted in this table is derived from the least squares fit of curves of the type shown in Figure 4. While these errors are small, the systematic error is much larger. A comparison of the P(4) and R(4) lines bears this out since the rate constants differ by a factor of two.

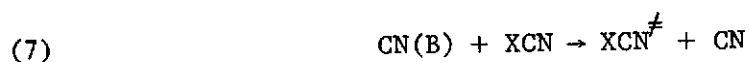
The quenching cross sections in Table 5 were calculated by dividing the rate constant by the relative collision velocity between a CN radical and C_2N_2 . The collision velocity was calculated assuming that the kinetic energy of the radicals had completely thermalized by the time the laser is pulsed. The time delay between the laser pulse and the flash lamp pulse is 100 μ sec. At C_2N_2 pressures of 10 to 500 microns the CN radical will have undergone 8 to 330 collisions with the C_2N_2 before the laser is turned on. This should be enough to thermalize the radical since the radical and C_2N_2 have comparable masses.

All of the known quenching cross sections of the B state of CN are summarized in Table 6. The quenching cross-section of the B state by C_2N_2 is of the same order of magnitude as the quenching by ICN and BrCN. In the work of Jackson and Faris¹² it was suggested that quenching occurred by excitation of ICN to a triplet state. Luk and Bersohn argued that since the quenching of the B state by BrCN and ICN was of the same order of magnitude, quenching could not be due to the triplet state since the reaction is endothermic for BrCN. They instead suggested that quenching occurred via,



This reaction however is endothermic by 2.4 e.v. for X equal to CN and would not be applicable for C_2N_2 .

Another possible reaction that would be exothermic for ICN, BrCN, and C_2N_2 would be the abstraction of either the X or CN component of the XCN by the B state radical. This is represented by reaction (7)



in which the new molecule may be internally excited. This reaction is analogous

to the halogen exchange reactions which have cross sections of the order of $5\text{-}20\text{\AA}^2$.¹⁴ The measured quenching cross sections for the B state radical by the cyanides is about a factor of two higher than those quoted for halogen exchange reaction. This is not surprising since the electron affinity of the B state of CN is higher than the electron affinity of CN¹⁵ in the X state. This will enhance the stability of the CN(B)---CN-CN complex¹⁶ leading to higher reaction cross sections through charge transfer interaction.

CONCLUSIONS

A new technique for measuring the lifetime of excited states of unstable species has been discussed. This technique is independent of the method of producing the radical. Application of this technique to the determination of the radiative lifetime of the $B^2\Sigma^+$ state yields lifetimes in substantial agreement with other measurements. The method yields the radiative lifetime of the individual rotational levels of the CN radical and is therefore capable of determining the presence of effects such as perturbation from other electronic states and predissociation. Observations of the lifetime of perturbed rotational levels of the $B^2\Sigma^+$ state of CN indicate that the lifetime of the $A^2\Pi$ state is of the order of several thousand nanoseconds rather than the hundred nanoseconds reported by Cook and Levy.

The quenching cross sections of the B state of CN by C_2N_2 is observed to be of the same magnitude as the quenching cross sections reported for ICN and BrCN. This suggests that the mechanism is the

the same for the three molecules. A mechanism for quenching which involves the abstraction of either the halogen atom or CN radical would be in agreement with the known results of B state quenching.

REFERENCES

1. H. S. Liszt and J.E. Hesser, *Ap. J.*, 159, 1101 (1970).
2. C.K. Luk and R. Bersohn, *J. Chem. Phys.*, 58, 2153 (1973).
3. T.J. Cook and D.H. Levy, *J. Chem. Phys.*, 57, 5059 (1972).
4. G. Herzberg, *Z. Phys.*, 49, 512 (1928).
5. T.W. Hansch, *Appl. Opt.*, 11, 895 (1972).
6. W. Braun and M. Lenzi, *Disc. of the Faraday Soc.*, 44, 252 (1967).
7. R.G. Bennett and F.W. Dalby, *J. Chem. Phys.*, 36, 399 (1962).
8. J.H. Moore and D.W. Robinson, *J. Chem. Phys.*, 48, 4870 (1968).
9. J.O. Arnold and R.W. Nicolls, *J. Quant. Spect. Rad. Tran.*, 13,
115 (1973).
10. H.E. Radford and H.P. Broida, *Phys. Rev.*, 128, 231 (1962).
11. D.L. Lambert, *Month. Not. Roy. Astron. Soc.*, 138, 213 (1968).
12. W.M. Jackson and J.L. Faris, *J. Chem. Phys.*, 56, 95 (1972).
13. J.A. Meyer and R.W. Nicholls, *Nature*, 225, 928 (1970).
14. Y.T. Lee, J.D. McDonald and D.R. Herschbach, *J. Chem. Phys.*, 49,
2447 (1968).
15. J. Berkowitz, W.A. Chupka and T.A. Walter, *J. Chem. Phys.*, 50,
1497 (1969).
16. Y.T. Lee, P.R. LeBreton, J.D. McDonald and D.R. Herschbach,
J. Chem. Phys., 51, 455 (1969).
17. T. Iwai, M.I. Savadatti, and H.P. Broida, *J. Chem. Phys.*, 47,
3861 (1967).
18. T. Wentink, Jr., L. Isaacson and J. Morreal, *J. Chem. Phys.*, 41,
278 (1964).
19. M. Jeunehomme, *J. Chem. Phys.*, 42, 4086 (1965).

TABLE 1

Radiative Lifetimes of the Rotational Levels of the Zeroth
Vibrational Level of the B State of CN

<u>Rotational Level*</u>	<u>τ (nsec) ($\pm 2\sigma$)</u>
P(0)	65.1 ± 0.8
P(1)	66.9 ± 0.5
P(2)	64.8 ± 0.6
P(3)	65.0 ± 0.6
P(4)	71.1 ± 0.3
P(5)	67.4 ± 0.4
P(6)	64.2 ± 0.7
P(7)	67.0 ± 0.7
P(8)	65.7 ± 0.8
P(9)	66.4 ± 0.5
P(10)	64.9 ± 0.3
P(11)	66.0 ± 0.4
P(12)	64.9 ± 0.4
P(13)	65.6 ± 0.4
P(14)	64.0 ± 0.3
R(4)	72.0 ± 0.8

The number in the parenthesis is the rotational quantum number (K') of the B state while the P and R refers to branch for which the lifetime was determined.

TABLE 2

Radiative Lifetime of CN ($B^2\Sigma^+$)

τ_0 (nsec)	Vibrational Level		Method	Source
85 \pm 10	0-4		Direct Decay (E.B.)	Bennett and Dalby
82 \pm 9	1		Phase Shift (E.B.)	Moore & Robinson
59.3 \pm 6	0-2		Phase Shift (E.B.)	Listz and Hesser
39.4 \pm 9.3	0		Anticrossing and Microwave linewidths	Cook and Levy
60.8 \pm 2	0		Direct Decay U.V. Photolysis	Luk and Bersohn
65.6 \pm 1.0	0	K' unperturbed	Direct Decay Laser Induced	This work

TABLE 3

Electronic f-values of the B State of CN

$f_{el}(\lambda)$	Experimental Method	Reference
0.035 ± 0.005	Shock tube (incident)	Arnold & Nicholls
0.034 ± 0.0005	Lifetime direct decay laser induced	This work
0.039 ± 0.004	Phase shift electron beam lifetime measurement	Liszt & Hesser
0.028 ± 0.003	Phase shift - rf discharge Lifetime measurement	Moore & Robinson
0.027 ± 0.003	Dissociative excitation by Electron Beam - direct decay	Bennett & Dalby
0.037 ± 0.001	Dissociative excitation by Photon impact - direct decay	Luk & Bersohn

TABLE 4

Computed and Observed Lifetimes of
 $CN(v'=0, K'=4, B^2_{\Sigma^+})$

τ_{π} (nsec)	τ observed (nsec)	τ computed (nsec)	$N_{\sigma p}/N_{\sigma}$	Reference
137	72 ± 1	68.1	0.86	(3)
396	72 ± 1	69.8	0.86	(17)
3500	72 ± 1	70.7	0.86	(18)
6430	72 ± 1	70.7	0.86	(19)
137	72 ± 1	68.3	1.00	(3)
396	72 ± 1	70.1	1.00	(17)
3500	72 ± 1	71.0	1.00	(18)
6430	72 ± 1	71.1	1.00	(19)

TABLE 5

Quenching Rate Constants and Cross Sections for the
Individual Rotational Levels in $\text{CN}(B^2\Sigma^+, v'=0)$

Line *	$k_{qK'} (\text{cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}) \times 10^{10}$	$Q(\text{\AA})^2$
P(0)	0.5 ± 0.1	8
P(1)	1.5 ± 0.1	22
P(2)	1.8 ± 0.1	29
P(3)	1.0 ± 0.1	16
P(4)	1.6 ± 0.1	26
P(5)	2.1 ± 0.1	34
P(6)	2.1 ± 0.1	34
P(7)	2.1 ± 0.1	34
P(8)	1.7 ± 0.1	27
P(9)	4.3 ± 0.2	69
P(10)	6.7 ± 0.1	108
P(11)	3.1 ± 0.1	50
P(12)	2.6 ± 0.2	42
P(13)	4.3 ± 0.1	69
P(14)	2.7 ± 0.1	44
R(4)	2.8 ± 0.2	49

* The number in the parenthesis is the rotational quantum number for the $B^2\Sigma^+$ state.

TABLE 6

Quenching Cross Sections Qq of the CN B² Σ^+ State

Qq	Quencher	Source
$41 \pm 20 \text{ \AA}^{\circ 2}$	C ₂ N ₂	This work
$46 \text{ \AA}^{\circ 2}$	ICN	Jackson and Faris (12)
$90 \text{ \AA}^{\circ 2}$	ICN	Myer and Nicholls (13)
$22.3 \text{ \AA}^{\circ 2}$	ICN	Luk and Bersohn (2)
$19.4 \text{ \AA}^{\circ 2}$	BrCN	Luk and Bersohn (2)
$12.2 \text{ \AA}^{\circ 2}$	CH ₄	Luk and Bersohn (2)
$11.0 \text{ \AA}^{\circ 2*}$	CH ₄	Jackson and Faris (12)
$25.3 \text{ \AA}^{\circ 2}$	O ₂	Luk and Bersohn (2)
$57.3 \text{ \AA}^{\circ 2}$	C ₂ H ₄	Luk and Bersohn (2)
$2.2 \text{ \AA}^{\circ 2}$	H ₂	Luk and Bersohn (2)
$9 \text{ \AA}^{\circ 2}$	CO	Luk and Bersohn (2)

* This is corrected for a lifetime of 65.6 nsec and for the arithmetic error made in the original paper.

FIGURE CAPTIONS

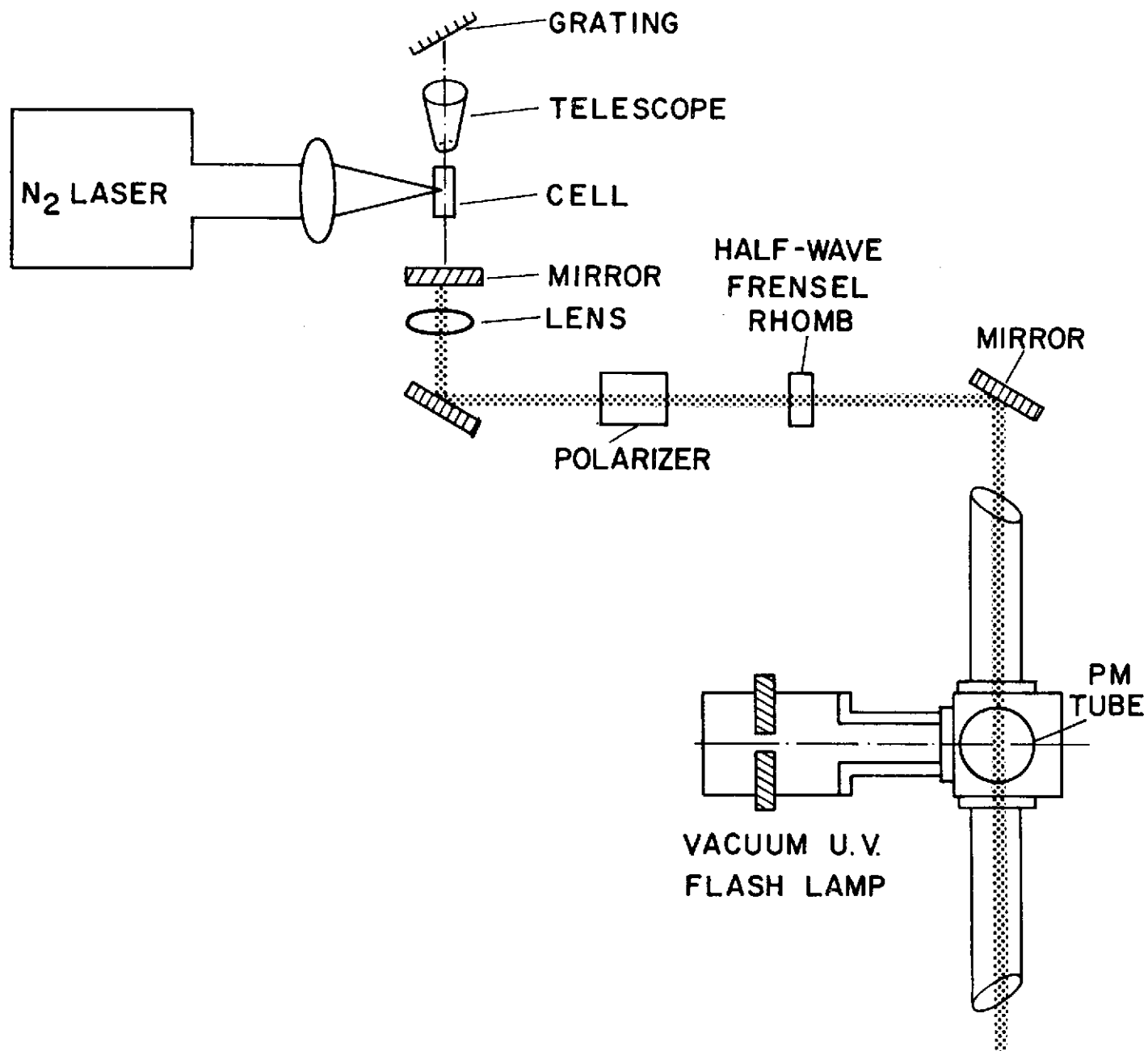
Figure 1. Experimental Apparatus.

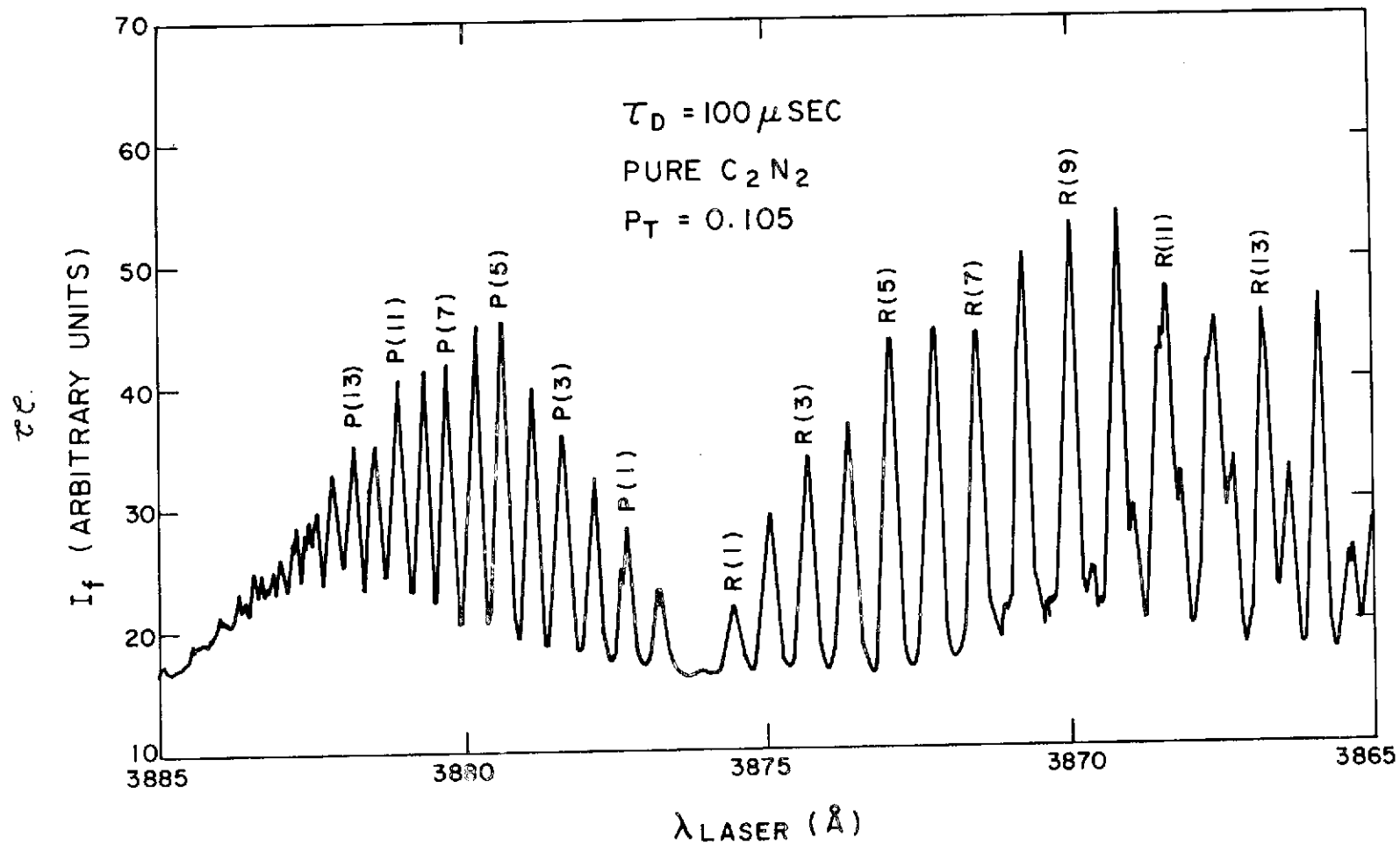
Figure 2. Photoluminescence Spectra of CN.

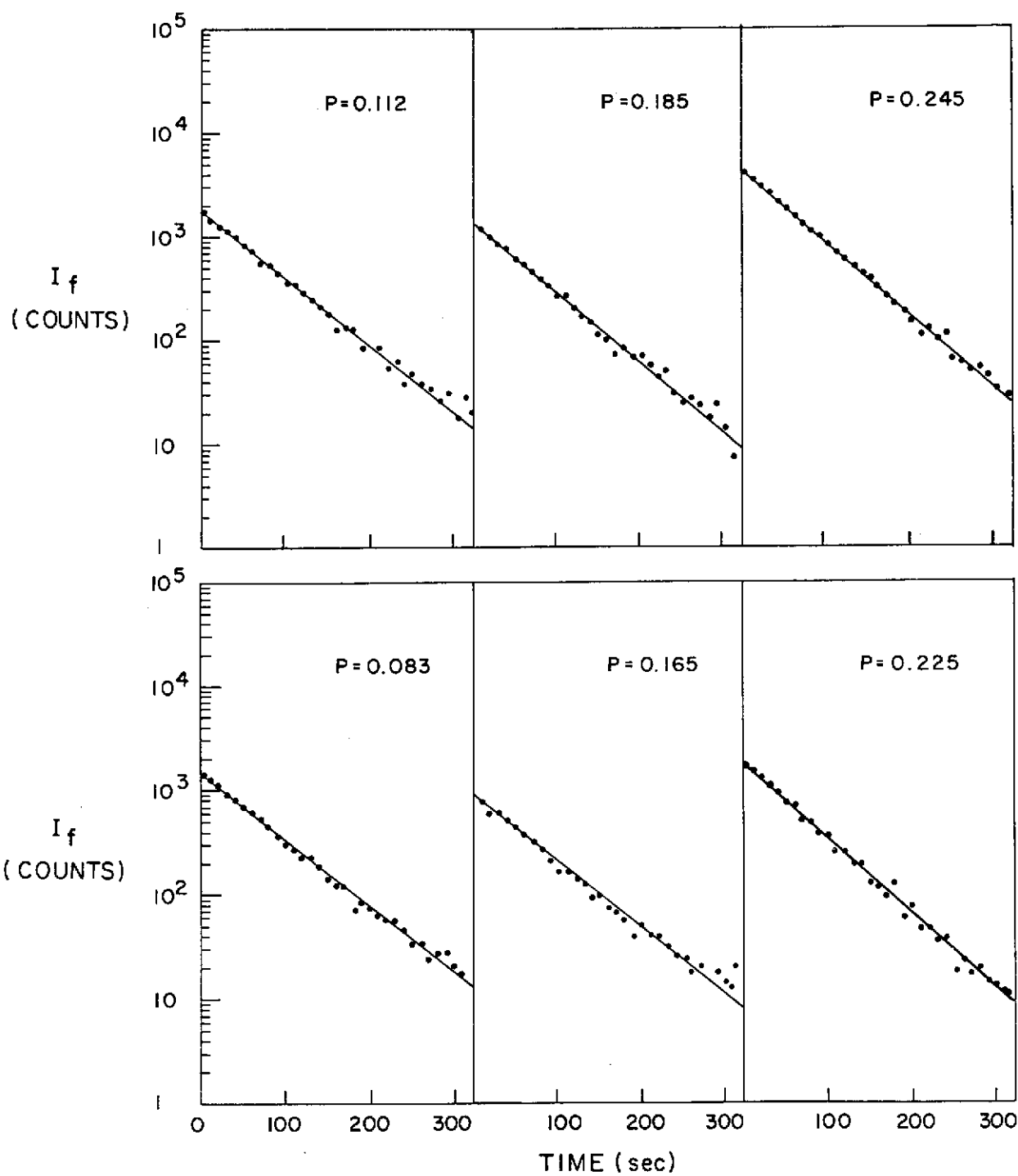
Figure 3. Decay Curves for the R(4) line.

Figure 4. Stern-Volmer Plot for R(4) line.

18







24

